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(54) Reflection of charged particles such as ions

(57) A surface is made reflective for charged particles such as ions by means of strong inhomogenous, RF alternating field patterns of low range. The inhomogenous alternating fields are generated by the application of an alternating voltage to a grid pattern. The elements of the pattern must be repeated periodically in the reflective surface; they are alternately connected with the poles of the RF voltage. The pattern may be a series of parallel rings defining a cylinder, or a cylindrical double helix 23, 24. With this invention, cylindrically shaped guidance systems for the transfer of ions in vacuum ranges of up to some to 10^{-2} millibar can especially be built. Also mass filters can be produced. The invention is a general extension of the known principles of RF multipole rod systems and of RF ion traps.

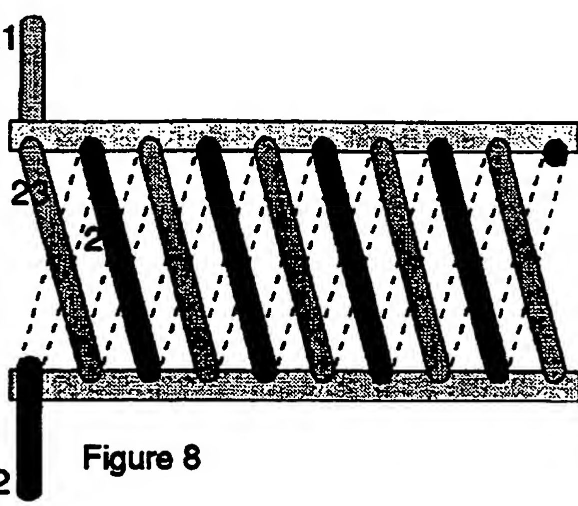

Figure 8

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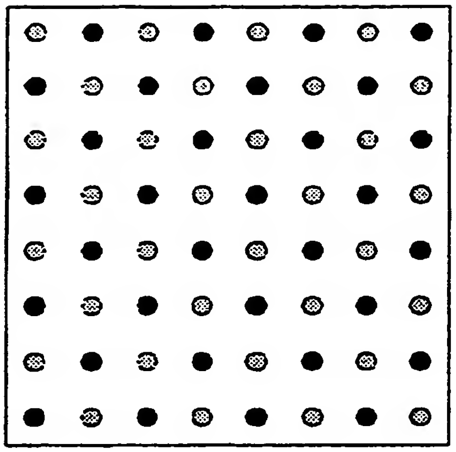

Figure 1

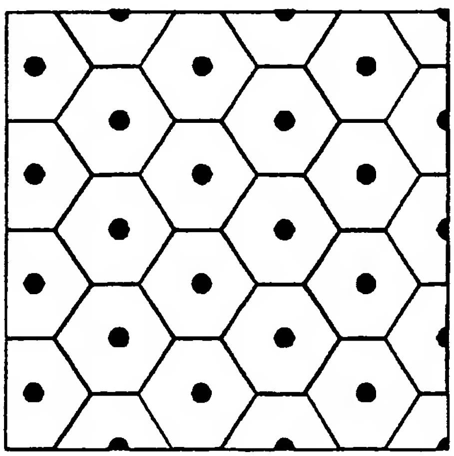

Figure 2

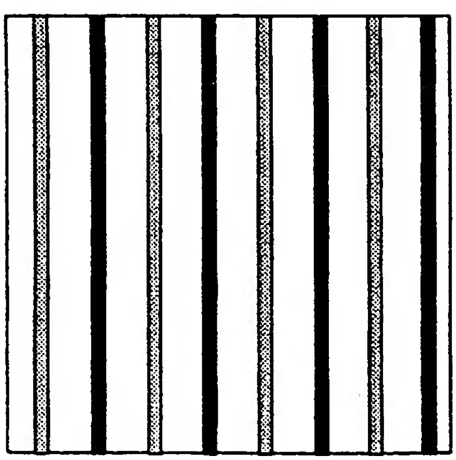

Figure 3

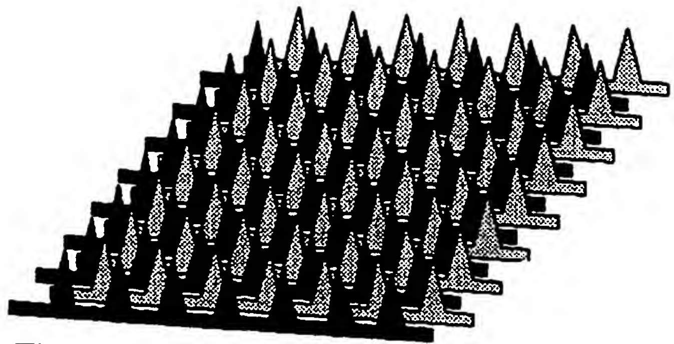

Figure 4

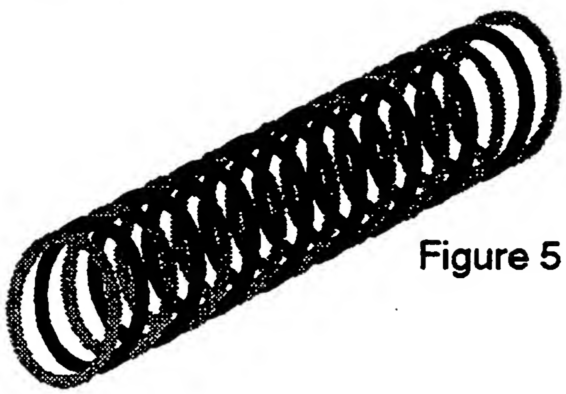

Figure 5

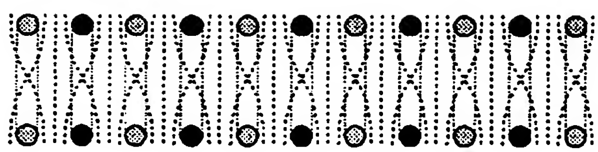

Figure 6

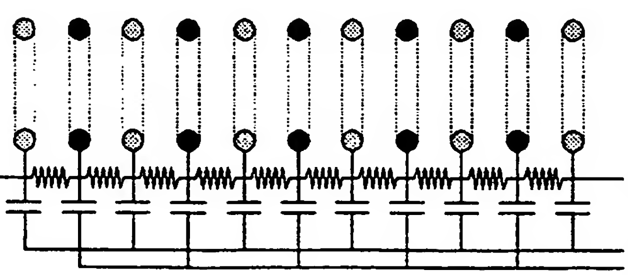

Figure 7

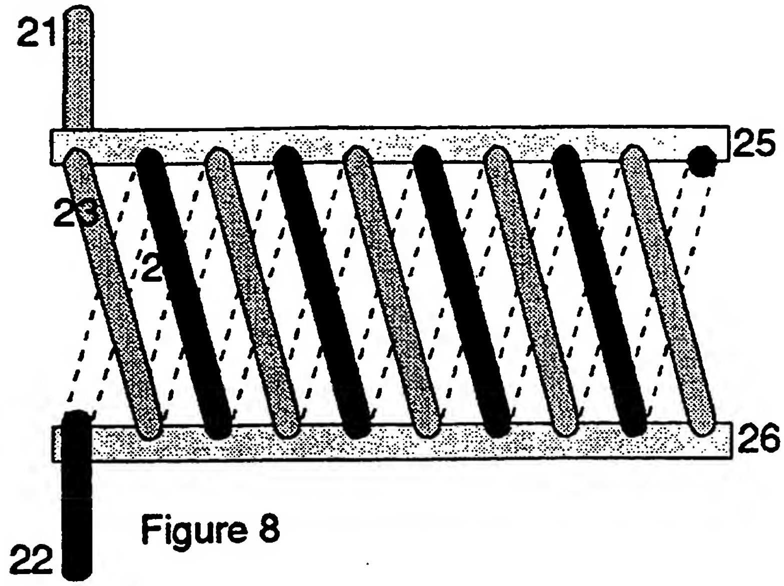

Figure 8

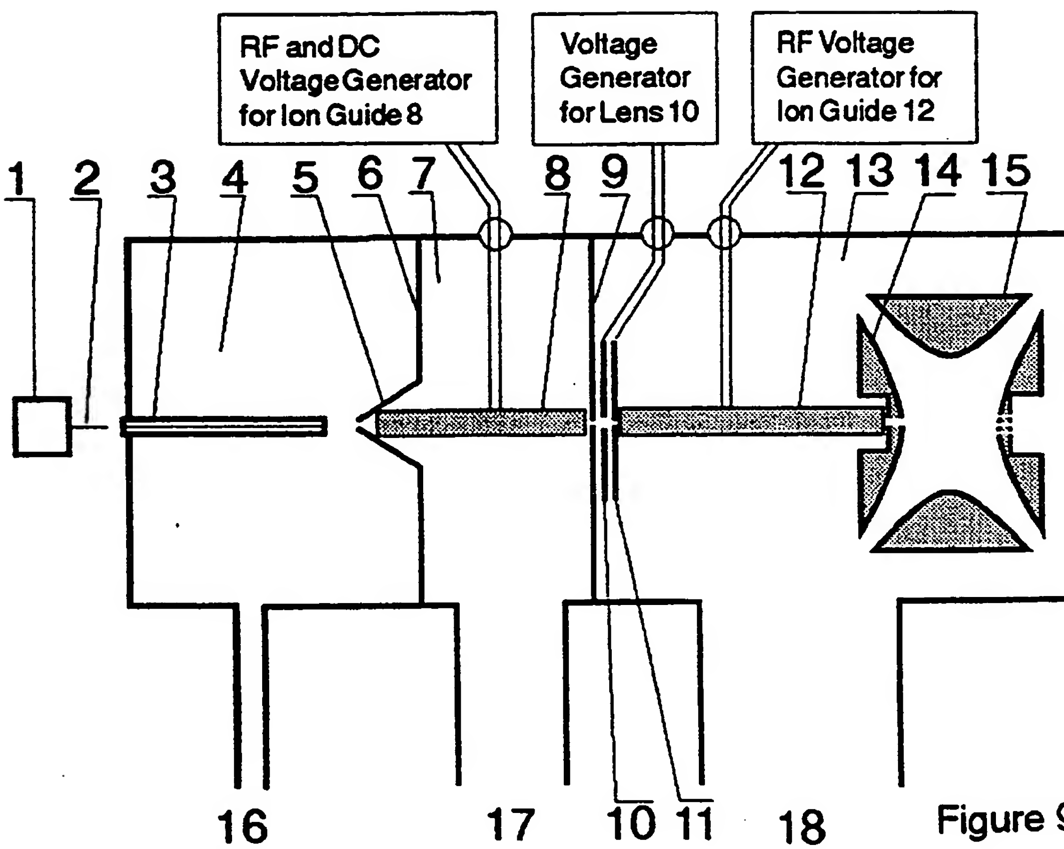

Figure 9

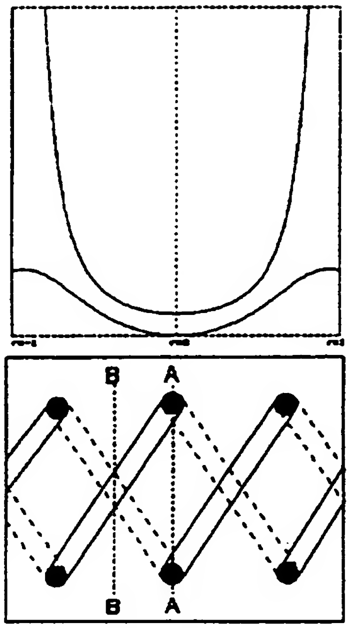

Figure 10

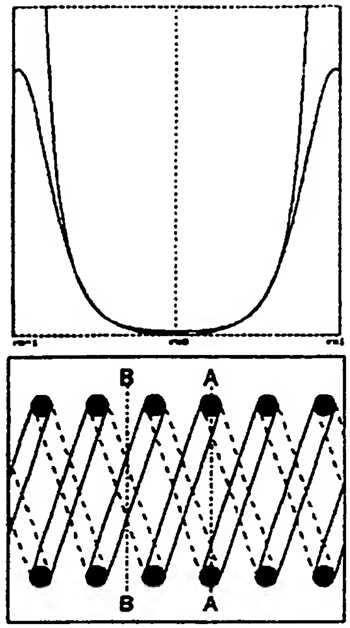

Figure 11

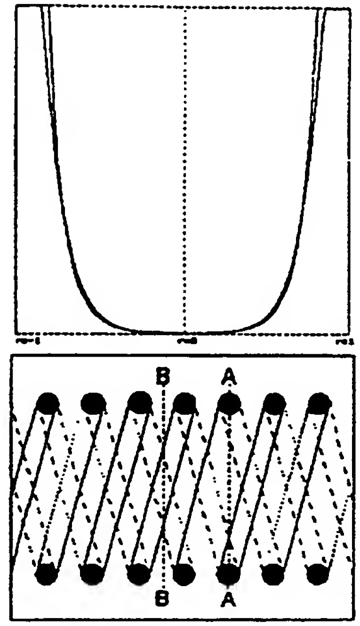

Figure 12

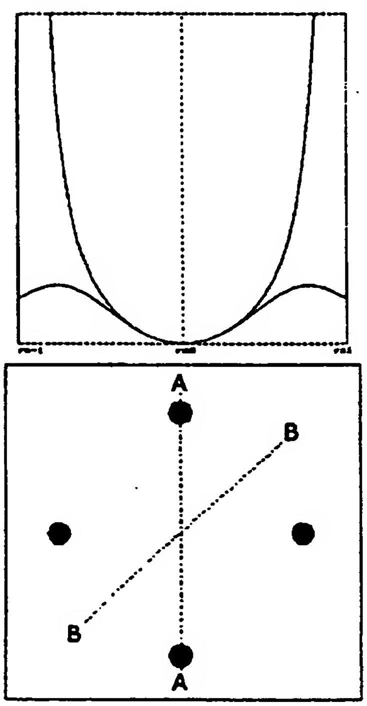

Figure 13

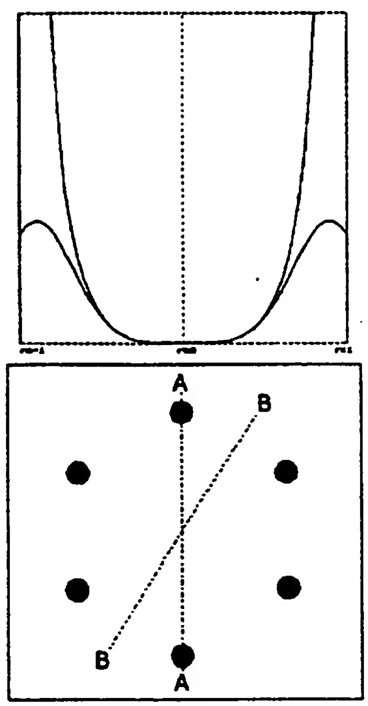

Figure 14

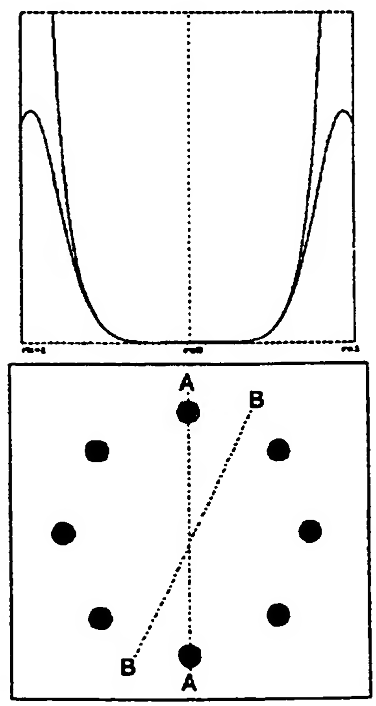

Figure 15

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Method and device for the reflection of charged particles at surfaces

The invention relates to methods and devices for the reflection of charged particles of any polarity and moderate kinetic energy on electric fields in front of reflective surfaces of any shape.

The invention consists of making the surface reflective for the charged particles through the use of extremely inhomogenous RF alternating field patterns of a relatively limited range. The inhomogenous alternating fields are generated by the application of alternating voltage to a grid pattern of electrodes. The grid elements of the pattern should periodically repeat themselves in the reflective surface; they are alternately connected with the phases of an RF voltage.

The invention can particularly be used to build cylindrically shaped guidance systems for the transfer of ions in vacuums up to several 10^{-2} millibar. Mass filters of a type not previously known can also be produced. The invention is a general extension of known principles for RF multipole rod systems and RF ion traps. In contrast to the multipole rod systems, the invention offers systems with simpler manufacturing and greater efficiency in the thermalization and guidance of moderately fast ions.

To store or guide ions within specially defined areas without using magnetic fields, it is necessary to reflect the ions on or in front of a wall surface without discharging them. Such reflections which preserve the ions have previously only been known for two and three dimensional RF multipole fields, which are an extension of the two or three dimensional RF quadrupole fields invented by Wolfgang Paul and Helmut Steinwedel. Therefore, for the guidance of ions over longer paths, only two dimensional RF multipole fields have been used up to now.

Two dimensional multipole fields consist of at least two rod pairs located on the surface of a cylinder, the rods of which are alternately supplied with both phases of an RF voltage. Two rod pairs are termed a two dimensional quadrupole field. More than two pairs of rods are hexapole, octopole, decapole, dodecapole etc. fields. The fields are called two dimensional because the same field distribution results in every cross section through the rod arrangement. The field distribution therefore only changes in two dimensions.

Three dimensional multipole fields are employed in so-called RF ion traps. They consist of at least one ring electrode and exactly two obligatory end cap electrodes. With one ring electrode between both end cap electrodes, a quadrupole field results, with two ring electrodes a hexapole field; three ring electrodes between the end cap electrodes create an octopole field, four ring electrodes generate a decapole field.

The RF multipole rod systems have been proposed as mass filters for inexpensive mass spectrometers, and as guidance fields for ions between the ion generator and ion user, particularly as an ion feeder for RF or ICR ion traps. As guidance fields, the multipole rod systems have especially favorable characteristics. Firstly, they are suitable for slowing down and thermalizing ions with moderately high velocities and wide distributions of velocity using a collision gas in the rod system (US 4 963 736); secondly, ions can be segregated above and below adjustable thresholds for the mass-to-charge ratios; and thirdly, ions can be temporarily stored in them using electric or gas dynamic reflectors on the ends of the rod system (US-A-5 179 278). This is particularly useful if ion traps are to be used as mass spectrometers for the analysis of substance ions. Ion trap mass spectrometers have a working period for the analysis of ions, during which no ions may be introduced. During this working phase, ions from the ion source can be decelerated, selected and collected, which allows an increase in utilization of the usually continuous ion sources.

In US-A-5 179 278, an estimate of the number of ions is also given which can be stored, taking space charge into account, in a quadrupole rod system.

In patent application GB9609812.4 (DE-A-19517507) a two dimensional pentapole field is proposed which consists of five parallel rods to which five phases of an RF rotational voltage are applied in a certain manner. This field can also be used for the guidance and temporary storage of ions.

Rod systems used for the guidance of ions are generally very slender and long, in order to concentrate ions in one area of very small diameter. They can then be operated advantageously at low RF voltages, creating a good starting point for further ion optical imaging of the ions. The clear cylindrical interior often has only 2 to 4 millimeters diameter, the rods are less than one millimeter thick, and the system is 10 to 15 centimeters long. The rods are usually fitted into grooves located inside ceramic rings. The requirements for uniformity of inside diameter, i.e. the distance between rods, are very high. The system is therefore not easy to produce and is additionally sensitive to vibrations. The rod systems bend quite easily and cannot then be adjusted.

This invention seeks to find methods and devices for the reflection of charged particles on or in front of a surface, thus making it possible to confine the particles in a space of any shape or to transport the particles in this space without any loss. The space does not need to be closed on all sides. Thus it can have openings, for example for the threading in and out of charged particles. The solution to the problem should be particularly suitable for building long and slender guidance fields with a hardwearing and robust mechanical structure. It should have good preconditions if possible for the thermalization of confined charged particles and also be able to be used as a mass filter.

In accordance with the invention inhomogenous electric alternating fields of short range are used for the repellent reflection of charged particles on a surface, which may be of any shape.

An alternating field at the tip of a wire, the field strength of which drops as generally known at $1/r^2$, or also the alternating field around a long wire that drops at $1/r$, reflect positively as well as negatively charged particles. The reason for this is the oscillation of the particle in the wire's alternating field. In this way it experiences, irrespective of its charge, its greatest repulsion from the wire exactly when it reaches the point of its oscillation at the smallest distance from the wire, meaning at the point of greatest field strength. The greatest attraction is when it is at the farthest point, meaning at the point of lowest field strength on its trajectory. Integrated over time, this produces a repulsion of the particle away from the tip. The repulsion field achieved through temporal integration can be described as a "pseudo potential", proportional to the square of the alternating field strength. Through derivation, a "pseudo force field" can be achieved from this. For the wire tip, the repellent pseudo potential drops at $1/r^4$, for the long wire at $1/r^2$ toward the outside, and it is inversely proportional to the mass of the ions and the square of the frequency.

If there are two adjacent wire tips which are connected with both opposing phases of an RF voltage, both tips each then repel charged particles. Their total effect is stronger. The alternating field of this dipole already drops more than only at $1/r^2$.

If an entire two dimensional field of wire tips is arranged where each adjacent tip in both dimensional directions is subjected to different phases of the RF voltage, a surface results which repels and thus reflects particles of both polarities at a short distance. This is not a specular (or regular), but rather a diffuse reflection. At a distance in front of this field, which is large in comparison to the distance between the tips, there is practically no more field effect.

Such a field of wire tips is relatively difficult to produce. However this is also not absolutely necessary. Even a field which radiates from long, parallel wires, also forms such an ion reflector if every second wire is subjected to one phase of RF voltage, while the remaining wires receive the other phase. A combination of tips and wires is also possible, somewhat like a mesh network in which a wire tip is found in every mesh.

A surface made of parallel wires also produces an alternating field which has only a short range in the area above the surface. The reflection is specular in the lengthwise direction of the wires, diffuse in the transverse direction. In an infinitely expanded arrangement, the field drops off almost exponentially toward the outside. With a field strength F at the surface of a rod which has a radius of one tenth of the distance between wires, D, there is only 5% of field strength F at a distance of one D, at a distance of two D only 0.2% of field strength F, at a distance of three D only 0.009% of field strength F. The repellent pseudo potential which is proportional to the square of this field strength therefore drops off even more sharply.

The known multipole rod systems represent a borderline case to the parallel wire arrangement. In this case the reflective surface is the surface of the cylinder on which the rods are arranged parallel to the axis of the cylinder and the number of axis-parallel rods is generally small. This well-known and much utilized borderline case is thus excepted from the claims to this invention.

With the help of this invention, other cylindrical arrangements for the guidance of charged particles can also be produced very easily. To do this, the reflecting surface just needs to be wound into a cylinder surface according to this invention. One can, for example, build a cylinder with wire tips pointing toward the inside, or a cylinder made of mesh with interspersed wire tips.

For a cylinder with a reflecting surface made of wires parallel to one another, several especially surprising solutions result from which only the axis-parallel arrangement of the rods, i.e. the two-dimensional multipole field, was known until now.

Thus a cylindrical guidance field can be created very simply from parallel wire rings, in which each adjacent wire ring is alternately subjected to both phases of RF voltage. The surface with parallel wires is in a way rolled up here in the direction of the wire to a cylinder. This arrangement of wire rings represents, from another perspective, an arrangement of lined-up quadrupole ion traps, whereby a small (although very shallow in its pseudo potential) quadrupole ion trap forms in the center of each ring. The pseudo potential wells of these ion traps become even shallower, the more closely the rings are pushed together (in relation to the diameter of the cylinder). Thus along the axis of the cylinder, a slightly rippled structure of the pseudo potential forms which is somewhat obstructive to the axial ion guidance. The axial components of the oscillations near the rings, particularly the diffuse reflection in the direction of the axis, is however advantageous for a rapid thermalization of axial velocity components of injected particles. Onto this cylindrical ring structure, yet another electrical field can be impressed in the axial direction through additional DC voltage on the rings, whereby propulsion of particles through the cylinder can be effected if desired.

An especially surprising solution results from a helical or coil-shaped arrangement of the wires. The entire grid structure can be produced, for example, from only two parallel wires, wound helically and double threaded around the cylinder. This arrangement has none of the ripple of the pseudo potential along the cylinder axis; rather it is completely straight and therefore especially suitable as a guidance field. The arrangement can be described as a "two wire coil" or "double helix". Both wires can easily be supplied with RF voltage at one end of the double helix by bending both wires here toward the outside and connecting them with the voltage supply. In this way the double helix does not form, as might first be expected, an electric choke which would prevent the rapid dispersion of the RF voltage. Since the resulting magnetic field disappears due to the opposing current flow from both phases of the RF

voltage, if both phases are fed into the double helix on the same side, the inductance of this arrangement also disappears. This structure also thermalizes the axial velocity components of the injected ions especially quickly. When using resistance wires with a supply of DC current, an axial DC field component can also be superimposed on this double helix, resulting in propulsion of the ions toward one end of the double helix. By switching this DC current on and off, propulsion of the ions can be controlled. The shape of the pseudo potential well in the double helix can be changed by altering the distance between the wires. With relatively large distance, a pseudo potential well results, the potential of which changes from the center to the cylinder wall by approximately r^2, making the pseudo potential well of a double helix similar to that of a linear quadrupole field. With narrower distance, a pseudo potential change can be generated somewhat proportional to r^4 or r^6; these arrangements more closely correspond to the pseudo potential wells from hexapole or octopole rod systems. This double helix or two-wire coil therefore has the great advantage of being able to be constantly fitted to a desired shape of pseudo potential well. It must also be noted that the shape of the pseudo potential well has great significance on the type of storage: in a r^2 potential, the ions collect in the axis, whereas with an r^6 potential well, they tend to remain outside near the wall due to the space charge repulsion.

Of course, according to this invention, coil-shaped arrangements can be produced from more than only one wire pair, creating something like a quadruple helix or sextuple helix. These will not be described in detail here.

All of these cylindrical arrangements, including those made up of electrode tips, rings or coils, have lower limits for the mass-to-charge ratios of the ions to be reflected, as already known from standard multipole rod arrangements. These cutoff limits can easily be determined experimentally. The lightweight ions are usually destroyed by hitting the wires.

Using a DC voltage which is superimposed onto the RF voltage, the upper range of the mass-to-charge ratios can also be limited. As is already done on the known quadrupole mass filter, an attractive potential which opposes the repellent pseudo potential of this wire is applied to every other wire in this way on wire arrangements. Since the pseudo potential is inversely proportional to the mass, the DC voltage attraction prevails for heavy masses, and the repulsion of the pseudo potential prevails for light masses. Thus the double helix can for example be used to very easily produce a mass filter for use as a mass spectrometer. Such a mass filter can however also be used advantageously for the preselection of ions when filling ion trap mass spectrometers.

All of these cylindrical arrangements can take the form of ion storage through two-sided attachment of apertures or ion lenses with reflecting voltages. However these only store ions of one polarity, while ion guidance is possible for both polarities. The apertures can also easily take the form of switching elements, allowing the ions to flow out at desired intervals.

Particularly advantageous are lens-like switching elements, rather in the shape of Einzel lenses. An additional electric DC field in the direction of the cylinder axis can reduce the emptying time.

A temporary store such as this offers advantages, especially for ion trap mass spectrometers, since the ions which are continually generated by an ion source can be collected and are not lost in times when the ion trap cannot be filled with ions. This applies to both RF quadrupole ion traps as well as ion cyclotron resonance traps.

The effect of these arrangements in different pressure and frequency ranges is determined by the gas friction and frequency which prevail in the arrangement. Thus, as has been known for decades, multiply charged macroscopic particles can be stored at normal atmospheric pressure if the frequencies are just reduced correspondingly to audio frequencies. Arrangements according to this invention will nevertheless be best operated in vacuum pressures below 10^{-1} millibar and at frequencies above 100 kilohertz, and preferably limited to ions as charged particles.

It is also possible to use the arrangement as a flat reflection grid for ions, switchable to ion transmission. The advantage in this is that ions of both polarity are reflected simultaneously when it is closed. The flat switchable grids currently used to-day do not reflect the ions but instead destroy them.

Description of the figures

Figure 1 shows a flush reflecting surface designed as a pattern of tips. The phases of the attached RF voltages are depicted by various shades of gray. Every tip with an RF phase is surrounded by four tips of the opposing phase. The resulting strongly inhomogenous field in front of the tips reflects ions of both polarities.

Figure 2 shows an ion guide consisting of parallel arranged rings. The rings are alternately connected to both phases of the RF voltage. The isolating holders for the rings and the metallic connections for the RF feed have been left out for reasons of improved clarity.

Figure 3 shows the potential distribution within the rings. In the center of every ring, a small quadrupole ion trap forms with the well-known potential characterics which overlap at an angle of $\mathrm{tg}\,\alpha = 1 : \sqrt{2}$. The quadrupole field is however limited to a very small area around the crossover area, and outside of the immediate center a complicated superimposition with higher, even multipole fields forms. The pseudo potential well of each ion trap is very high in a radial direction, however very shallow in an axial direction, since the next ion traps are connected up right away in both axial directions.

Figure 4 illustrates how an axial DC field can be superimposed on the ring system by using electrical connections, in order to give ion movement within the system a preferred direction. The RF is fed via capacitors to the rings for this purpose. The rings are connected to one

another via resistance chokes, through which the RF voltage cannot flow. However a weak DC current flows over the chokes, which in this way supplies the rings with a constantly dropping DC voltage which generates the DC field. By switching off the DC current, propulsion of the ions can be switched off.

Figure 5 shows the double helix made from two helically coiled wires, 23 and 24. The RF voltage is applied via feeders 21 and 22. The coiled wires 23 and 24 are glued into the grooves of two ceramic holders 25 and 26, thus maintaining their stability.

Figure 6 shows the application of two devices according to this invention used in one arrangement with a quadrupole ion trap as a mass spectrometer which receives the ions from an external electrospray ion source. Supply tank one contains a liquid which is sprayed using an electrical voltage between the fine spray capillary 2 and the end surface of entrance capillary 3. The ions are introduced through entrance capillary 3 together with ambient air into the differentially first pump chamber 4, which is connected via nozzle 16 to a fore-pump. The ions are accelerated toward skimmer 5 and enter through the aperture in skimmer 5, which is located in partition 6, into the second chamber 7 of the differential evacuation system. This chamber 7 is connected via the pump nozzle 17 with a fore-pump. The ions are received in this chamber by the cylindrical ion guide 8, constructed according to this invention, which terminates at wall 9 between the second differential pump chamber 7 and the high vacuum chamber 13. This ion guide takes the form of a relatively tightly wound double helix, in order to be able to store ions in a large volume, and is supplied with an RF voltage, which can be superimposed by a DC current as necessary from an electrical supply unit. In this way, ions can be selected within a narrow range of mass-to-charge ratios for storage. In wall 9, there is a small aperture which forms an Einzel lens together with apertures 10 and 11. The drawing potential at the center aperture 10 punches through the hole in the wall 9 and removes thermalized ions from the first double helix 8 by suction when it is switched to admission. The ions entering into the high-vacuum chamber 13 are guided through a second double helix 12 to the ion trap mass spectrometer, which consists of end cap electrodes 14 and the ring electrode 15. This double helix 12 is wound with greater spacing of the wires so that the ions are kept close to the axis, enabling them to thread through the small hole in end cap 14 better. The high-vacuum chamber 13 is evacuated via pump nozzle 18.

Figure 10 to 15 show the pseudo potentials wells in double helices of different slopes (figures 10, 11, 12) compared with pseudo potentials in multipole rod systems (figures 13, 14, 15). The potential wells are shown in each case for cross section lines from grid element to grid element (A-A), and for cross section lines drawn through the gaps between neighboring grid elements (B-B). The pseudo potential wells of the helices are shown for distance-to-radius ratios equal to 1.5 (figure 10), 0.8 (figure 11) and 0.6 (figure 12), respectively, compared

with those of quadrupole (figure 13), hexapole (figure 14), and octopole (figure 15) rod systems.

Particularly favorable embodiments

A reflective surface for ions of both polarities, according to this invention, has the shortest range of the RF field when it is designed as a pattern of tips, as shown in Figure 1. For this, the tips do not need to be so sharp, as can be seen in Figure 1. A tip radius is sufficient which corresponds to about one tenth to one fifth of the distance of tips from one another. Then the RF voltage is not as great for the same reflective effect as when using very sharp tips, however the lower mass cutoff limit is then increased.

For many purposes however, the range of the RF fields must not necessarily be limited to the smallest values. For the ion guide in cylindrical devices, there is a great advantage in the ability to adjust the range and therefore the shape of the pseudo potential well to an optimum. This adjustability is especially prevalent with wires, since their distances are very easily selectable and can be suited to the problem. The wire distancing can be freely selected both on the arrangement with parallel rings, and on the double helix, determining the shape of the pseudo potential well as described above.

The ion guide made up of parallel rings has the slight disadvantage that this arrangement forms a sequence of quadrupole ion traps, even if their pseudo potential well depths are not really deep, and the wells are rather more than shallow puddles. When emptying this ion guide by means of simple outflow, some ions remain behind in these puddles. This disadvantage can however be easily remedied by superimposing a DC field on the structure which drives the ions out of the puddles. The electrical connection for such a superimposition is shown in Figure 4. For rings with 5 millimeter diameter, small resistance chokes of 10 microhenry and 100 ohms are best used, the capacities being 100 picofarads. However since this method, which offers advantages for certain purposes, generally means a complication, the embodiment of an ion guide as a double helix will be particularly emphasized in the following, since this puddle formation is not known there.

The ion guide in the shape of a double helix can very easily be produced, forming a robust structure that is very resistant to mechanical damages and vibrations. Ion guides advantageously have a small diameter; the diameter of the open, cylindrical space in the interior is often only selected to be three to six millimeters in size. The length, according to requirements stemming from the geometry of the pump connections, is around 5 to 15 centimeters. The narrow diameter serves to concentrate the ions; it however also permits RF supplies at far lower voltages, so that RF generators with direct transistor outputs can be used. Elaborate transformers tuned to the capacities of the ion guide are not needed then. With

direct transistor outputs, the frequency can also be controlled much more easily over wide ranges.

Using a double-threaded screw as the helix core, which can easily be made for this purpose on a lathe, both wires of the double helix can very easily be wound, by inserting the wires in both threads of the double-threaded screw. Here it is advantageous if the threads are less than half as deep as the wire diameter. Hard, springy wire can be coiled by winding it first on a thinner, smooth core and then stretching, so that practically no winding tension occurs if wound to the double-threaded screw. A well usable double helix with four millimeter inside diameter is made up of hard nickel-chromium or stainless steel wires, 0.6 millimeter diameter, and spaced one millimeter from one another. Therefore one winding is 3.2 millimeters high. Then 2, 3 or even 4 approximately one millimeter small, isolating holder strips, 25 and 26, are glued onto the windings 23 and 24, while the windings are still on the screw core. These holder strips 25 and 26 can be manufactured from glass, ceramic or even plastic. The holder strips have round grooves, obliquely milled, which correspond to the diameter spacing and pitch of the wires. Due to the gluing, a very solid structure results, because the already hard wires are each attached in this way with a small spacing of a maximum of a half rotation to each other, as seen in Figure 5. After the adhesive has hardened, the screw core, which was lightly greased beforehand, can be unscrewed out of the structure.

On both wire connections 21 and 22 of the double helix, an RF voltage with a frequency between 2 and 6 megahertz and a voltage between 40 and 600 volts is normally applied. The result of this is bottom cutoff masses of singly charged ions which are variable between about 10 to 1,000 atomic mass units. The exact cutoff mass is dependent upon the distance of the wire from one another and must be experimentally determined. The lower the voltage, the lower the cutoff limit is, these being directly proportional. The frequency also determines the cutoff mass, the latter being inversely proportional to the square of the frequency.

A superimposition of the RF voltage with a proportional DC voltage of up to about 100 volts results in a limitation of the mass range from above. With a correctly shaped and faultless double helix, a single mass can be filtered out. Then only this mass remains in the ion guide. In order not to carry the process tolerances for the double helix too far, one should limit oneself to a range with this filtration which encompasses several masses, and then make the final isolation of a single mass, if desired, in the ion trap.

A DC field with axial alignment can also be superimposed onto the double helix. To do this it is necessary to use resistance wires for the double helix, and to send DC current through both wires. The outflow of RF into the DC power supply can be prevented quite well although with RF chokes. The DC field thus generated is in general only small, however a field of only

0.1 volts per centimeter already provides a very strong drive for the ions to flow out of the double helix.

It is however also possible to generate propulsion of the ions toward one end in a completely different way. However this drive is permanent and cannot be switched off. To do this, the double helix wires must be wound around a slightly conical core. The conical form automatically provides propulsion toward the end with the greater diameter, so that the ions especially collect at the wider end during storage and can also easily be removed from there.

In the following, one application for such ion guides in the form of double coils in a mass spectrometer will be described. The application relates to Figure 6. Here two ion guides, each in the form of a double helix, are in use. The embodiment relates to an RF quadrupole ion trap made up of two end cap electrodes 11 and a ring electrode 12, taking the form of a mass spectrometer. Both ion guides here serve to thermalize the ions and provide temporary storage on the one hand, and simple ion guidance on the other. The application should however not be solely designed for this purpose. Also the use of the RF quadrupole ion trap as a mass spectrometer described here should not be inferred as limited, and for other types of use for ion traps or for other types of ion trap or any other type of mass spectrometer, an expert can easily make the suitable adjustments.

An RF quadrupole ion trap consists of a ring electrode and two end cap electrodes arranged axially to that. Filling up with ions occurs through a hole in one of the end caps. An ion trap mass spectrometer is only filled with ions over a brief time. There then generally follows a damping period in which the ions are collected in a small cloud in the center of the ion trap. If a normal mass spectrum is to be scanned, a period then follows in which the ions are ejected mass by mass from the ion trap and measured with a measuring device. The ejection generally occurs through the end cap of the ion trap which faces the injection end cap. For other modes of operation, for example MS/MS, other periods of ion isolation and fragmentation are inserted. The filling period is therefore generally brief in comparison to the sum of the other periods. Ions generated in the ion source during the time outside the filling period are usually distorted and useless for analysis. With the mechanically simple and robust device according to this invention, it is possible to temporarily store these ions, to condition them for a subsequent analysis and thus make better use of them for analysis.

The embodiment described here is presented with an electrospray ion source outside the vacuum housing of the mass spectrometer. The invention should not however be expressly limited to this type of ion generation. The electrospray ion source consists of a supply tank 1 for a liquid, in which molecules of the analysis substance have been detached. The ions are produced in the electrospray ion source by spraying fine droplets of liquid into air (or nitrogen) from a fine spray capillary 2 under the influence of a strong electrical field,

whereby the droplets evaporate and leave their charge on detached molecules. In this way, very large molecules can be ionized easily.

The ions from this ion source are usually introduced through an inlet capillary 3 with an inside diameter of about 0.5 millimeters and a length of about 100 millimeters into the vacuum of the mass spectrometer. They are entrained by the simultaneously inflowing air (or by another gas introduced to the area around the entrance) through gas friction. A differential pump device with two intermediate chambers 4 and 7 takes over evacuation of the resulting gas. The ions entering through the capillary are accelerated within the first chamber 4 of the differential pump device in the adiabatically expanding gas jet, and pulled through an electrical field to the facing aperture of a gas skimmer 5. The gas skimmer 5 is a conical tip with a central hole, whereby the outer cone wall deflects the inflowing gas toward the outside. The aperture of the gas skimmer guides the ions, now with much less accompanying gas, into the second chamber 7 of the differential pump device.

Directly behind the aperture of skimmer 5, the first ion guide 8 begins. This consists of a double helix wound with very narrow distancing, in order to prepare a relatively large volume for the storage of ions with a broad potential well. The inside diameter is, at 4 millimeters, quite small however, so that the double helix can reach far into the cone of the skimmer, and that the required RF voltages remain small.

The wires are supplied with RF voltage. Frequency and voltage of the RF are selected in such a way that a desired bottom mass cutoff limit for the ions is attained. Ions beneath this cutoff limit are not retained in the double helix. In this way, undesired ions of small masses can be removed, such as ions from the solvent or admixtures to the solvent used in the electrospray ion source.

With a frequency of about 6 megahertz and a voltage of about 250 volts, all singly charged ions in the double helix with masses above 50 atomic mass units are focused. Lighter ions, for example the air ions N_2^+, O_2^+, escape the ion guide. Through higher voltages or lower frequencies, the cutoff limit for ion masses can be raised to any values up to about 1,000 atomic mass units. The exact function of the lower mass cutoff limit in conjunction with voltage and frequency is determined experimentally by a calibration process.

Using a selectable superposition of RF voltage with a DC voltage, the mass range can also be limited toward heavy masses, and under favorable conditions the mass range can be limited to one single mass. In this way ions of single masses are readily preselected. The mass range can also be determined by a calibration procedure and made reproducible for use.

Experience shows that ions which enter through a skimmer hole with 1.2 millimeter diameter, are accepted by this ion guide practically without any loss if their mass is above the cutoff

limit. This unusually good acceptance rate can be primarily traced to the gas dynamic conditions at the entrance aperture.

The double helix 8 leads from the aperture in gas skimmer 5, which is arranged as part of the wall 6 between the first 4 and second chamber 7, through this second chamber up to the small aperture in wall 9. In this chamber 7, there is preferably a vacuum of some 10^{-3} millibar, in order to cause rapid thermalization of the ions accelerated to the gas.

By changing the axis potential of the double helix 8 in comparison to the potentials of the skimmer 5 and the wall 9, the ion guide 8 can be used for storage of ions of one polarity, therefore either for positive or negative ions. The axis potential is identical with the zero potential of the RF voltage on the wires of the double helix. The stored ions run back and forth constantly in the ion guide 8 and are slowed down by collisions with the residual gas in the chamber 7. Since they attain a velocity of about 500 to 1,000 meters per second or more during the adiabatic acceleration phase, they first run through the length of the ion guide several times per millisecond. With a residual gas vacuum of some 10^{-3} millibar, the ion movements are thermalized in a few seconds both in a radial and axial direction.

The calmed ions collect in the axis of the ion guide. Due to the potential well which is steep toward the walls, but very shallow near the axis, the ions nevertheless spread themselves out rapidly within a larger volume due to their mutual coulombic repulsion.

Due to a drawing voltage at the center lens aperture 10, a potential punch-through arises through the aperture 9 into the double helix 8, which can be adjusted in such a way that ions can flow out. The outflow is supported by the space charge. The ions passing through are, as in this example, transported through the second double helix 12 to the mass spectrometer. This double helix 12 has a greater wire distance and therefore a narrower potential well. Therefore the ions remain very well near the axis and can then be introduced well into the ion trap. The wall of the ion trap end cap 14 has an injection hole for the ions with a diameter of 1.5 millimeters.

By changing the potential at the center lens aperture 10, the ions can be made to flow out either through the second double helix 12 into the ion trap, or remain stored in the first double helix 8.

The second double helix 12 can of course be replaced by other types of ion guidance. Thus a quadrupole rod system can be used here, however the known ion guide made up of one tube with a central wire, both at corresponding potentials.

The ion source can be coupled especially with devices for sample separation, for example with capillary electrophoresis. Capillary electrophoresis then provides time-delayed substance batches of brief duration in high concentration. The temporary storage of ions in the first double helix 8 can then be very favorably used in order to store ions of one substance for

several fillings of the ion trap, whereby numerous MS/MS analyses of daughter ion spectra of different parent ions are possible. Even MS/MS/MS analyses with granddaughter ion spectra can be performed; the latter are of particular interest for the amino acid sequence analysis of proteins. The electrophoresis run can easily be interrupted for longer-lasting analyses by switching off the voltage temporarily.

The RF quadrupole ion trap 14, 15 need not necessarily take the form of a mass spectrometer. It can for example serve to collect ions for time-of-flight spectrometers, to concentrate them into a dense cloud, and to then outpulse them into the flight path of the time-of-flight spectrometer. At the same time it is also possible, before outpulsing the ions, to isolate or also to fragment certain desired ions in the ion trap first in the usual way, therefore attaining MS/MS measurements in time-of-flight spectrometers. The advantage of the time-of-flight spectrometer lies in its large mass range and rapid spectral scanning.

Even the transfer of ions from an ion source to an ion cyclotron resonance mass spectrometer can be presented advantageously with storage ion guides designed by the ideas of this invention. The ICR spectrometer is subject to similar work cycles as an RF quadrupole ion trap, and therefore the storageability of the ion guide in the analysis phases is of great advantage. Even the thermalization of ions has an advantageous effect. The ion guide does not in general reach up to the storage cell of the spectrometer here, and the magnetic field takes over continued guidance of the ions.

If for purposes of better time resolution one wishes to empty the storage ion guide 8 very quickly into the ion trap, one can give the ions a constant additional push in the direction of the ion trap by a slightly conical design of the double helix, for example 4 millimeter diameter at the input end and 6 millimeters on the ion trap end, incrementally.

In another embodiment, the double helix 8 can also store all ions above the mass cutoff limit while the double helix 12 first takes on the preselection of mass. This type of operation is then of interest if all ions of a chromatographic or electrophoretic substance batch are to first be stored and then analyzed. Then the masses of the available ion types could be determined in a first spectrum, in order to then preselect these masses in further analysis phases in the double helix 12 and analyze them in detail in the mass spectrometer.

Switchable help for the emptying of the double helix can be attained by the superimposition with an axis-parallel DC field, as has already been described above. Here it depends upon the operating requirements of the ion source whether all temporarily stored ions are to be loaded into the ion trap each time or not.

However, of course, ion sources which are inside the vacuum housing of the mass spectrometer can be connected via storage ion guides according to this invention to ion traps. Here too, ions from time-separated substance peaks, such as result during couplings with

chromatographic or electrophoretic methods, can be stored for several analyses in the ion trap.

The mass spectrometer does not even need to be an ion trap mass spectrometer. The transfer of ions, and especially the thermalization, is also advantageous for other types of mass spectrometers. These could be, for example, quadrupole or sector field mass spectrometers.

Due to this invention, however, completely different devices can also be created. For example, bulging containers for the storage of ions can also be produced. These can easily be made by joining two truncated cones. The ions can then be made useful through a stronger, superimposed DC field.

The temporary storage of ions can also be used particularly well for ion-molecule reactions.

Large-surface switchable grids for ions of both polarities can also be produced.

Claims

1. A device for the reflection of charged particles by means of an electrical force field in front of a reflective surface, wherein the surface comprises a plurality of electrodes arranged in a periodic pattern in the surface, and an RF generator connected to respective electrodes in the pattern, such that adjacent electrodes are connected with different phases of the RF alternating voltage from the RF generator,
provided that the electrodes are not arranged in the form of a plurality of parallel rods disposed on the surface of a cylinder, and further provided that if the electrodes are arranged in the form of four or fewer generally parallel rings, the arrangement does not also include electrode end caps..

2. A device as claimed in Claim 1, wherein the reflective surface is in the shape of a cylinder or truncated cone, and wherein the periodic electrode pattern consists of at least one pair of wires which are coiled within the surface of a cylinder or a truncated cone.

3. A device as claimed in Claim 1 or claim 2, wherein the periodic electrode pattern takes the form of exactly one pair of wires are coiled in the shape of a double helix.

4. A device as claimed in any one of the preceding claims, wherein the device is used as an admission filter for ions of a desired range of mass-to-charge ratios, by superposition of a DC voltage on the RF voltage.

5. A device as claimed in any one of the preceding claims, wherein the device is provided with end surfaces having apertures or ion lenses, and wherein the apertures or ion lenses are connected to a DC voltage supply.

6. A device as claimed in any one of the preceding claims, wherein the device is filled with a collision gas at a pressure of from 10^{-4} to 10^{-1} millibar.

7. A device as claimed in any one of the preceding claims, wherein the device is arranged between an ion generator and an ion-using device.

8. A device as claimed in Claim 7, wherein the ion-using device is a mass spectrometer.

9. A method for the reflection of charged particles from a surface by means of an electrical force field, which method comprises providing a plurality of electrodes arranged in a periodic pattern in the surface, and applying an RF voltage to respective electrodes in the pattern, such that adjacent electrodes are connected with different phases of the RF alternating voltage,
provided that the electrodes are not arranged in the form of a plurality of parallel rods disposed on the surface of a cylinder, and further provided that if the electrodes are arranged in the form of three or fewer generally parallel rings, the arrangement does not also include electrode end caps.

10. A method as claimed in Claim 9, wherein the periodic pattern of electrodes takes the form of a two dimensional point grid made up of electrode stubs, which project into the reflective surface from one side and end there.

11. A method as claimed in Claim 9, wherein the periodic pattern of electrodes is constructed from a mesh grid and a point grid made up of electrode stubs, wherein each electrode stub is located inside the mesh.

12. A method as claimed in Claim 9, wherein the periodic pattern of electrodes consists of electrode wires which run parallel to one another in the reflective surface.

13. A method as claimed in any one of claims 9 to 12, wherein the reflective surface takes the form of the surface of a cylinder or a truncated cone.

14. A method as claimed in Claim 13, wherein the periodic pattern of electrodes consists of parallel rings which are each generally transverse to the axis of the cylinder or truncated cone.

15. A method as claimed in Claim 14, wherein, as well as the RF phases which alternate from ring to ring, a DC potential is also applied to the rings,which changes from ring to ring along the axis.

16. A method as claimed in Claim 13, wherein the periodic pattern consists of at least one pair of wires which are wound in a coil around the axis of the cylinder or truncated cone.

17. A method as claimed in Claim 16, wherein exactly one pair of wires is used which are wound in the shape of a double helix.

18. A method as claimed in Claims 16 or Claim 17, including the step of tuning the RF and DC voltage amplitude in order to permit the selective passage of particles within a range of specific mass-to-charge ratios.

19. A method as claimed in Claims 17 or Claim 18, wherein an axial DC field is generated by current through the wires of the double helix.

20. A method as claimed in any one of Claims 13 to 19, wherein the arrangement is used for the guidance of ions along the axis of the cylinder or truncated cone.

21. A method as claimed in any one of Claims 13 to 20, wherein the cylindrical or truncated-cone-shaped arrangement is used for ion storage by means of reflectors on the end surfaces, at least one of which is switchable.

22. A method as claimed in any one of Claims 13 to 21, wherein a collision gas is provided at a pressure of from 10^{-4} to 10^{-1} millibar for the thermalization of fast ions.

23. A method as claimed in any one of Claims 13 to 22, wherein the cylindrical or truncated-cone-shaped arrangement is used for the transfer of ions from an ion generator to an ion-using device.

24. A method as claimed in Claim 23, wherein the ion using device is a mass spectrometer.

25. A method as claimed in Claim 24, wherein the mass spectrometer contains an ion trap.

26. A method as claimed in any one of Claims 23 to 25, wherein the arrangement is used for the storage of substance ions of a chromatographically or electrophoretically separated substance batch.

27. A device for the reflection of charged particles by means of an electrical force field in front of a reflective surface, wherein the surface comprises a plurality of electrodes arranged in a periodic pattern in the surface, and an RF generator connected to respective electrodes in the pattern, such that adjacent electrodes are connected with different phases of the RF alternating voltage from the RF generator,
provided that the electrodes are not arranged in the form of a plurality of parallel rods disposed on the surface of a cylinder, and further provided that if the electrodes are arranged in the form of generally parallel rings, the arrangement does not also include electrode end caps..

28. Method for the reflection of charged particles on an electrical force field in front of a reflective surface, wherein a periodic pattern of electrically conductive grid elements is located on the reflective surface, and adjacent grid elements are each alternately connected with phases of an RF alternating voltage and optionally with a superimposed DC voltage; here the already well-known multipole rod systems with axis parallel rods and the also well-known multipole ion traps made up of rings and end caps should be excepted.

29. Device for the reflection of charged particles on an electrical force field in front of a reflective surface, consisting of an electrode pattern in the surface and an RF generator, wherein the electrode pattern consists of a periodic ensemble of electrically conductive elements, and wherein each adjacent grid element is alternately connected with different phases of the RF alternating voltage from the RF generator; here the already well-known multipole rod systems with axis parallel rods and the also well-known multipole ion traps made up of rings and end caps should be excepted.

The Patent Office

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Application No:	GB 9613692.4	**Examiner:**	Martyn Dixon
Claims searched:	all	**Date of search:**	23 September 1996

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Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): H1D (DHC,DMAA,DMC,DMD,DME,DMG,DMH)

Int Cl (Ed.6): H01J (49/02,49/06,49/34,49/40,49/42)

Other: online: WPI, INSPEC

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
A	GB 1293148 A	(Varian)	1,9,27-29
X	GB 0725113 A	(Philips) see the double helix 4	1-5,7-9, 12,13, 16-20,23, 24,27-29
X	WO 92/14259 A	(Kirchner) see parallel electrode sheets 12 and page 22, lines 3 et seq	1,4-9, 12-15, 20-29

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
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